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(54) Title: CATALYST AND A PROCESS USING THE CATALYST

(57) Abstract: A catalyst which comprises a carrier and silver deposited on the carrier, which carrier has a surface area of at least 1 m²/g, and a pore size distribution such that pores with diameters in the range of from 0.2 to 10 µm represent at least 70 % of the total pore volume and such pores together provide a pore volume of at least 0.27 ml/g, relative to the weight of the carrier; a process for the preparation of a catalyst which process comprises depositing silver on a carrier, wherein the carrier has been obtained by a method which comprises forming a mixture comprising: a) from 50 to 90 %w of a first particulate a-alumina having an average particle size (d₅₀) of from more than 10 up to 100 µm; and b) from 10 to 50 %w of a second particulate a-alumina having an average particle size (d₅₀) of from 1 to 10 µm; %w being based on the total weight of a-alumina in the mixture; and shaping the mixture into formed bodies and firing the formed bodies to form the carrier, and a process for the epoxidation of an olefin, which process comprises reacting an olefin with oxygen in the presence of a said catalyst.

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the carrier such as alkali metals and some forms of silica can have a beneficial effect.

Intuitively it might also be considered that the higher the surface area of the carrier, the greater the area available for deposition of the silver and therefore the more effective the silver deposited thereon. However, this is generally found not to be the case and in modern catalysts the tendency is to use a carrier with a surface area of less than 1 m²/g.

10 SUMMARY OF THE INVENTION

The present invention teaches that the picture with respect to carrier surface area is significantly more complicated than was at first appreciated since the nature of the porosity of the carrier, in particular the pore size distribution and the pore volume provided by the pores which have a pore size within a defined range, has now been found to play a significant role. On this basis it was possible to prepare olefin epoxidation catalysts with excellent activity, selectivity and unusually prolonged retention of the activity and stability level. The carriers having an advantageous pore size distribution may be made from particulate materials which have specific particle sizes.

The present invention provides a catalyst which comprises a carrier and silver deposited on the carrier, which carrier has a surface area of at least 1 m²/g, and a pore size distribution such that pores with diameters in the range of from 0.2 to 10 μm represent at least 70 % of the total pore volume and such pores together provide a pore volume of at least 0.27 ml/g, relative to the weight of the carrier.

The invention also provides a process for the preparation of a catalyst which process comprises:

a) selecting a carrier which has a surface area of at

The invention also provides a process for the epoxidation of an olefin, which process comprises reacting an olefin with oxygen in the presence of a catalyst which has been obtained by a process which comprises depositing silver on a carrier, wherein the carrier has been obtained by a method which comprises forming a mixture comprising:

- a) from 50 to 90 %w of a first particulate α -alumina having a d_{50} of from more than 10 up to 100 μm ; and
- b) from 10 to 50 %w of a second particulate α -alumina having a d_{50} of from 1 to 10 μm ;

%w being based on the total weight of α -alumina in the mixture; and firing the mixture to form the carrier. In an embodiment, amongst others, the mixture may be shaped into formed bodies and the formed bodies are fired to form the carrier. When the formed bodies are formed by extrusion, it may be desirable to include conventional burnout materials and/or extrusion aids, and an aqueous liquid, e.g. water, in the mixture.

The invention also provides a method of using an olefin oxide for making a 1,2-diol, a 1,2-diol ether or an alkanolamine comprising converting the olefin oxide into the 1,2-diol, the 1,2-diol ether or the alkanolamine wherein the olefin oxide has been obtained by a process for the epoxidation of an olefin in accordance with this invention.

In accordance with the teaching of this invention, by maximizing the number of pores having a diameter in the range of 0.2 to 10 μm , in particular by minimizing the number of pores having a diameter greater than 10 μm , the catalyst is advantaged over catalysts where are prepared from carriers which have a substantial number of pores having a diameter greater than 10 μm .

typically requires 5 minute sonification when using the Horiba LA900 particle size analyzer.

As used herein, pore volume (ml/g), surface area (m²/g) and water absorption (g/g) are defined relative to the weight of the carrier, unless stated otherwise.

Typically, the pore size distribution is such that pores with diameters less than 0.2 μ m represent less than 10 % of the total pore volume. Typically, the pore size distribution is such that pores with diameters greater than 10 μ m represent less than 20 %, in particular less than 15 %, of the total pore volume. Preferably, the pore size distribution is such that the pores with diameters in the range of from 0.2 to 10 μ m represent more than 75 %, in particular more than 80 %, more preferably more than 85 %, most preferably more than 90 % of the total pore volume; the pores with diameters greater than 10 μ m represent less than 12 %, in particular less than 10 %, more in particular less than 5 % of the total pore volume; and the pores with diameters less than 0.2 μ m represent less than 7 %, in particular at most 5 %, and more in particular at most 4 % of the total pore volume.

Frequently, the pore size distribution is such that the pores with diameters in the range of from 0.2 to 10 μ m represent less than 99.9 %, more frequently less than 99 % of the total pore volume; the pores with diameters greater than 10 μ m represent more than 0.1 %, more frequently more than 0.5 % of the total pore volume; and the pores with diameters less than 0.2 μ m represent more than 0.1 %, more frequently more than 0.5 % of the total pore volume.

Typically, the pores with diameters in the range of from 0.2 to 10 μ m provide a pore volume of at least 0.28 ml/g, in particular at least 0.3 ml/g, more in particular at least 0.35 ml/g. Typically, the pores with

absorption and higher total pore volume, the carrier, or the catalyst made therefrom, may have lower crush strength.

The carrier may be based on a wide range of materials. Such materials may be natural or artificial inorganic materials and they may include refractory materials, silicon carbide, clays, zeolites, charcoal and alkaline earth metal carbonates, for example calcium carbonate. Preferred are refractory materials, such as alumina, magnesia, zirconia and silica. The most preferred material is α -alumina. Typically, the carrier comprises at least 85 %w, more typically 90 %w, in particular 95 %w α -alumina, frequently up to 99.9 %w α -alumina.

Carriers may generally be made by firing particulate mineral components at an elevated temperature until the particles sinter together. In general, firing is continued until the particles are bonded together, either by the formation of bond posts from any added bond material or through sintering, but preferably not beyond the point at which the water absorption of the carrier is reduced.

The water absorption of the carrier may suitably be controlled by the use of so-called burnout materials, and it is preferred to employ a burnout material when practicing this invention. Burnout materials are well known in the art (cf., for example, F F Y Wang (Ed.), "Treatise on Materials Science and Technology", Volume 9, (New York, 1976), pp. 79-81; or J S Reed, "Introduction to the Principles of Ceramic Processing", (New York, 1988), pp. 152 ff.). The burnout materials may also be used to ensure the preservation of the structure during a green, i.e. unfired, phase of the carrier preparation, for example the phase in which formed bodies are shaped, for example by extrusion. The burnout materials are removed during the firing. The use of burnout materials also allows more complete sintering without too great a

in view of the careful matching of large and small particles of the α -alumina components. The alumina particles are readily commercially available, or they may readily be made, for example, by subjecting more course materials to grinding and sieving operations. In an embodiment, the smaller particles may be prepared from the larger particles by grinding, and the ground and un-ground particles are then combined. In another embodiment, the desired mixture of large and small particles may be formed by grinding relatively large particles to the extent that the mixture of particles has the desired bimodal particle size distribution.

Typically, the first particulate α -alumina is employed in a quantity of from 65 to 75 %w, relative to the total weight of α -alumina in the mixture. Typically, the second particulate α -alumina is employed in a quantity of from 25 to 35 %w, relative to the total weight of α -alumina in the mixture.

In particular when the carrier is an α -alumina carrier, more in particular comprising at least 80 %w, 90 %w, or 95 %w α -alumina, it is preferred that the bond material is based on a silica-containing composition comprising a crystallization inhibitor, inhibiting the formation of crystalline silica-containing compositions. It is also preferred that the bond material provides a coating of a non-crystalline silica compound to the carrier surface.

Typically, silica-containing compositions for use as a bond material comprise an amorphous silica compound which may be, for example, a silica sol, a precipitated silica, an amorphous silica, or an amorphous alkali metal silicate or aluminasilicate. Typically, silica-containing compositions for use as a bond material may also comprise hydrated alumina. The crystallization inhibitor that is most

the mixture;

d) from 0.2 to 0.8 %w of an amorphous silica compound, as specified hereinbefore, calculated as silicon oxide relative to the total weight of α -alumina in the mixture; and

5 e) from 0.05 to 0.3 %w, of an alkali metal compound, calculated as the alkali metal oxide relative to the total weight of α -alumina in the mixture;

and then shaping the mixture into formed bodies and firing the formed bodies at a temperature of from 1250 to 1500 °C

10 to form the carrier.

The preferred alumina hydrate is boehmite, though gibbsite, bayerite or diaspore may also be used.

Suitable alkali metals are, for example, lithium, sodium and potassium, or combination thereof. Suitable
15 alkali metal compounds are, for example, alkali metal carbonates, alkali metal acetates, alkali metal formates, alkali metal nitrates, and combinations thereof. Typically, the overall atomic ratio of silicon to the alkali metal is in the range of from 1 to 10, more typically 2 to 8, for
20 example 6. The overall atomic ratio of silicon to the alkali metal is deemed to relate to the total alkali metal content and the total silicon content of the carrier, which includes any alkali metal and any silicon which may be present in the carrier other than in the bond material.

25 It is also preferred that the carrier particles be prepared in the form of formed bodies, the size of which is in general determined by the dimensions of a reactor in which they are to be deposited. Generally however it is found very convenient to use particles such as formed bodies
30 in the form of powdery particles, trapezoidal bodies, cylinders, saddles, spheres, doughnuts, and the like. The cylinders may be solid or hollow, straight or bend, and they

bond posts formed from the bond material, if incorporated in the mixture. Generally, drying may take place between 20 and 400 °C and preferably between 30 and 300 °C, typically for a period of up to 100 hours and preferably for from 5 minutes to 50 hours. Typically, drying is performed to the extent that the mixture contains less than 2 %w of water. Generally, firing may take place between 1250 and 1500 °C, typically between 1250 and 1470 °C, preferably between 1300 and 1450 °C, more preferably between 1300 and 1440 °C, typically for a period of up to about 5 hours and preferably for from 2 to 4 hours. Drying and firing may be carried out in any atmosphere, such as in air, nitrogen, or helium, or mixtures thereof. Preferably, in particular when the formed bodies contain organic material, the firing is at least in part or entirely carried out in an oxidizing atmosphere, such as in oxygen containing atmosphere.

It has been found that the performance of the catalyst may be enhanced if the carrier is washed, to remove soluble residues, before deposition of other catalyst ingredients on the carrier. On the other hand, unwashed carriers may also be used successfully. A useful method for washing the carrier comprises washing the carrier in a continuous fashion with hot, demineralised water, until the electrical conductivity of the effluent water does not further decrease. A suitable temperature of the demineralised water is in the range of 80 to 100 °C, for example 90 °C or 95 °C. Reference may be made to WO-00/15333 and US-B-6368998, which are incorporated herein by reference.

Generally, the catalyst of this invention comprises silver as a catalytically active metal. Appreciable catalytic activity is obtained by employing a silver content of the catalyst of at least 10 g/kg, in particular at least 50 g/kg, relative to the weight of the catalyst. The

Group IA metals are selected from lithium, potassium, rubidium and cesium. Most preferably the Group IA metal is lithium, potassium and/or cesium. Preferably the Group IIA metals are selected from calcium and barium. Where
5 possible, the further element may suitably be provided as an oxyanion, for example, as a sulfate, borate, perrhenate, molybdate or nitrate, in salt or acid form.

It is preferred to employ the carrier of this invention in the preparation of a highly selective catalyst. The
10 highly selective silver-based catalysts may comprise, in addition to silver, one or more of rhenium, molybdenum, tungsten, a Group IA metal, and a nitrate- or nitrite-forming compound, which may each be present in a quantity of from 0.01 to 500 mmole/kg, calculated as the element
15 (rhenium, molybdenum, tungsten, the Group IA metal or nitrogen) on the total catalyst. The nitrate- or nitrite-forming compounds and particular selections of nitrate- or nitrite-forming compounds are as defined hereinafter. The nitrate- or nitrite-forming compound is in particular a
20 Group IA metal nitrate or a Group IA metal nitrite. Rhenium, molybdenum, tungsten or the nitrate- or nitrite-forming compound may suitably be provided as an oxyanion, for example as a perrhenate, molybdate, tungstate or nitrate, in salt or acid form.

25 Of special preference are the highly selective catalysts which comprise rhenium in addition to silver. Such catalysts are known from EP-A-266015, US-A-4761394 and US-A-4766105, which are incorporated herein by reference. Broadly, they comprise silver, rhenium or compound thereof,
30 the further element (as defined hereinbefore, in particular tungsten, molybdenum and/or a Group IA metal, in particular lithium and/or cesium) other than rhenium or compound thereof, and optionally a rhenium co-promoter. The rhenium

Although the present epoxidation process may be carried out in many ways, it is preferred to carry it out as a gas phase process, i.e. a process in which the feed is contacted in the gas phase with the catalyst which is present as a solid material, typically in a packed bed. Generally the process is carried out as a continuous process.

The olefin for use in the present epoxidation process may be any olefin, such as an aromatic olefin, for example styrene, or a di-olefin, whether conjugated or not, for example 1,9-decadiene or 1,3-butadiene. Typically, the olefin is a monoolefin, for example 2-butene or isobutene. Preferably, the olefin is a mono- α -olefin, for example 1-butene or propylene. The most preferred olefin is ethylene.

The olefin concentration in the feed may be selected within a wide range. Typically, the olefin concentration in the feed will be at most 80 mole%, relative to the total feed. Preferably, it will be in the range of from 0.5 to 70 mole%, in particular from 1 to 60 mole%, on the same basis. As used herein, the feed is considered to be the composition which is contacted with the catalyst.

The present epoxidation process may be air-based or oxygen-based, see "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd edition, Volume 9, 1980, pp. 445-447. In the air-based process air or air enriched with oxygen is employed as the source of the oxidizing agent while in the oxygen-based processes high-purity (at least 95 mole%) oxygen is employed as the source of the oxidizing agent. Presently most epoxidation plants are oxygen-based and this is a preferred embodiment of the present invention.

The oxygen concentration in the feed may be selected within a wide range. However, in practice, oxygen is generally applied at a concentration which avoids the flammable regime. Typically, the concentration of oxygen

compounds are nitro compounds, nitroso compounds, amines, nitrates and nitrites, for example nitromethane, 1-nitropropane or 2-nitropropane. In preferred embodiments, nitrate- or nitrite-forming compounds, e.g. nitrogen oxides
5 and/or organic nitrogen compounds, are used together with an organic halide, in particular an organic chloride.

The reaction modifiers are generally effective when used in low concentration in the feed, for example up to 0.1 mole%, relative to the total feed, for example from
10 0.01×10^{-4} to 0.01 mole%. In particular when the olefin is ethylene, it is preferred that the reaction modifier is present in the feed at a concentration of from 0.1×10^{-4} to 50×10^{-4} mole%, in particular from 0.3×10^{-4} to 30×10^{-4} mole%, relative to the total feed.

15 In addition to the olefin, oxygen and the reaction modifier, the feed may contain one or more optional components, such as carbon dioxide, inert gases and saturated hydrocarbons. Carbon dioxide is a by-product in the epoxidation process. However, carbon dioxide generally
20 has an adverse effect on the catalyst activity. Typically, a concentration of carbon dioxide in the feed in excess of 25 mole%, preferably in excess of 10 mole%, relative to the total feed, is avoided. A concentration of carbon dioxide as low as 1 mole% or lower, relative to the total feed, may
25 be employed. Inert gases, for example nitrogen or argon, may be present in the feed in a concentration of from 30 to 90 mole%, typically from 40 to 80 mole%. Suitable saturated hydrocarbons are methane and ethane. If saturated hydrocarbons are present, they may be present in a quantity
30 of up to 80 mole%, relative to the total feed, in particular up to 75 mole%. Frequently they are present in a quantity of at least 30 mole%, more frequently at least 40 mole%.

The olefin oxide produced in the epoxidation process may be converted into a 1,2-diol, a 1,2-diol ether, or an alkanolamine. As this invention leads to a more attractive process for the production of the olefin oxide, it

5 concurrently leads to a more attractive process which comprises producing the olefin oxide in accordance with the invention and the subsequent use of the obtained olefin oxide in the manufacture of the 1,2-diol, 1,2-diol ether, and/or alkanolamine.

10 The conversion into the 1,2-diol or the 1,2-diol ether may comprise, for example, reacting the olefin oxide with water, suitably using an acidic or a basic catalyst. For example, for making predominantly the 1,2-diol and less 1,2-diol ether, the olefin oxide may be reacted with a ten fold
15 molar excess of water, in a liquid phase reaction in presence of an acid catalyst, e.g. 0.5-1.0 %w sulfuric acid, based on the total reaction mixture, at 50-70 °C at 1 bar absolute, or in a gas phase reaction at 130-240 °C and 20-40 bar absolute, preferably in the absence of a catalyst.
20 If the proportion of water is lowered the proportion of 1,2-diol ethers in the reaction mixture is increased. The 1,2-diol ethers thus produced may be a di-ether, tri-ether, tetra-ether or a subsequent ether. Alternative 1,2-diol ethers may be prepared by converting the olefin oxide with
25 an alcohol, in particular a primary alcohol, such as methanol or ethanol, by replacing at least a portion of the water by the alcohol.

The conversion into the alkanolamine may comprise, for example, reacting the olefin oxide with ammonia. Anhydrous
30 or aqueous ammonia may be used, although anhydrous ammonia is typically used to favour the production of monoalkanolamine. For methods applicable in the conversion of the olefin oxide into the alkanolamine, reference may be

5. 0.1 pbw of sodium oxide (in the form of sodium acetate).

To this mixture were added 5 %w, relative to the mixture weight, of petroleum jelly and 9 %w, relative to the mixture weight, of burnout material and 0.1 %w, relative to the mixture weight, of boric acid. Water (about 30 %w, relative to the mixture weight) was then added in an amount to make the mixture extrudable and this mixture was then extruded to form formed bodies in the form of hollow cylinders that are about 8 mm in diameter and 8 mm long. These were then dried and fired in a kiln at 1425 °C, for 4 hours in air to produce Carrier A. As regards procedures followed in this carrier preparation, reference may be made to US-A-5100859.

15 A second carrier (hereinafter "Carrier B") was made by the same procedure as Carrier A, except that 14 %w of burnout material was used, instead of 9 %w.

A third carrier (hereinafter "Carrier C") was made by the same procedure as Carrier A, except that:

- 20 - 20 pbw of the α -alumina with d_{50} of 3 μm was used instead of 29 pbw;
- 76.4 pbw of an α -alumina with d_{50} of 16 μm was used, instead of the α -alumina with d_{50} of 28 μm ;
- 8 %w of burnout material was used, instead of 9 %w; and
- 25 - 14 %w, relative to the mixture weight, of the petroleum jelly was used, instead of 5 %w.

For comparative purposes, an α -alumina was prepared according to the process as described in Example 1 of US-A-5100859 (hereinafter "Carrier D").

30 The carriers exhibited characteristics as indicated in Table I. The pore size distribution is specified as the volume fraction (%v) and the volume (ml/g) of the pores having diameters in the specified ranges (< 0.2 μm , 0.2-

TABLE I

Carrier	Surface area (m ² /g)	Water absorption (g/g)	Pore volume (ml/g)	Pore size distribution		
				<0.2 μm (%v)	0.2- 10 μm (%v; ml/g)	>10 μm (%v)
A	2.04	0.42	0.41	5	92; 0.37	3
B	2.11	0.49	0.42	9	72; 0.30	19
C	2.51	0.55	0.56	3	95; 0.53	2
D *)	0.73	0.40	0.40	< 1	64; 0.26	36
*) comparative						

Preparation of catalysts

A silver-amine-oxalate stock solution was prepared by
5 the following procedure:

415 g of reagent-grade sodium hydroxide were dissolved
in 2340 ml de-ionized water and the temperature was adjusted
to 50 °C.

1699 g high purity "Spectropure" silver nitrate was
10 dissolved in 2100 ml de-ionized water and the temperature
was adjusted to 50 °C.

The sodium hydroxide solution was added slowly to the
silver nitrate solution, with stirring, while maintaining a
solution temperature of 50 °C. This mixture was stirred for
15 15 minutes, then the temperature was lowered to 40 °C.

Water was removed from the precipitate created in the
mixing step and the conductivity of the water, which
contained sodium and nitrate ions, was measured. An amount

centrifugation at 500 rpm for two minutes. The catalyst pre-cursor was then dried while being shaken at 250 °C for 5.5 minutes in a stream of air.

The catalysts were used to produce ethylene oxide from ethylene and oxygen. To do this, 1.5 to 2 g of crushed catalyst were loaded into a stainless steel U-shaped tube. The tube was immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The weight of catalyst used and the inlet gas flow rate (0.28 Nl/minute) were adjusted to give a gas hourly space velocity of 6800 Nl/(l.h), as calculated for un-ground bulk catalyst. The inlet gas pressure was 1530 kPa.

The gas mixture passed through the catalyst bed, in a "once-through" operation, during the entire test run including the start-up, consisted of 25 %v ethylene, 7 %v oxygen, 5 %v carbon dioxide, 63 %v nitrogen and 2.0 to 6.0 ppmv ethyl chloride.

The initial reactor temperature was 180 °C and this was ramped up at a rate of 10 °C per hour to 225 °C and then adjusted so as to achieve a constant ethylene oxide content of 1.5 %v in the outlet gas stream at an ethyl chloride concentration of 2.5 ppmv. Performance data at this conversion level are usually obtained when the catalyst has been on stream for a total of at least 1-2 days.

The initial performance values for selectivity and temperature are reported in Table II, below. A lower temperature needed to accomplish a certain ethylene oxide content in the outlet gas stream is indicative for a higher activity of the catalyst.

30

CLAIMS

1. A catalyst which comprises a carrier and silver deposited on the carrier in a quantity of at least 10 g/kg, relative to the weight of the catalyst, which carrier has a surface area of at least 1 m²/g, and a pore size distribution such that pores with diameters in the range of from 0.2 to 10 μm represent at least 70 % of the total pore volume and such pores together provide a pore volume of at least 0.27 ml/g, relative to the weight of the carrier.

2. A catalyst as claimed in claim 1 wherein the carrier has a pore size distribution such that the pores with diameters in the range of from 0.2 to 10 μm represent more than 75 % of the total pore volume and such pores together provide a pore volume of at least 0.28 ml/g, relative to the weight of the carrier; the pores with diameters greater than 10 μm represent less than 20 % of the total pore volume; and the pores with diameters less than 0.2 μm represent less than 10 % of the total pore volume.

3. A catalyst as claimed in claim 2 wherein the carrier has a pore size distribution such that the pores with diameters in the range of from 0.2 to 10 μm represent more than 90 % of the total pore volume and such pores together provide a pore volume of at least 0.3 ml/g, relative to the weight of the carrier; the pores with diameters greater than 10 μm represent less than 10 % of the total pore volume; and the pores with diameters less than 0.2 μm represent less than 7 % of the total pore volume.

4. A catalyst as claimed in any of claims 1-3 wherein the carrier has a total pore volume in the range of from 0.28 to 0.8 ml/g and a surface area of at most 2.9 m²/g, in particular the carrier has a total pore volume in the range

11. A catalyst as claimed in claim 9 or 10 wherein the Group IA metals are selected from lithium, potassium, rubidium and cesium.

12. A process for the preparation of a catalyst as claimed in any of claims 1-11, which process comprises:

5 a) selecting a carrier which has a surface area of at least $1 \text{ m}^2/\text{g}$, and a pore size distribution such that pores with diameters in the range of from 0.2 to $10 \text{ }\mu\text{m}$ represent at least 70 % of the total pore volume and such pores

10 together provide a pore volume of at least 0.27 ml/g , relative to the weight of the carrier, and

b) depositing at least silver on the carrier in a quantity of at least 10 g/kg , relative to the weight of the catalyst.

13. A process for the preparation of a catalyst which process comprises depositing silver on a carrier, wherein the carrier has been obtained by a method which comprises forming a mixture comprising:

15

a) from 50 to 90 %w of a first particulate α -alumina having an average particle size (d_{50}) of from more than $10 \text{ }\mu\text{m}$ up to $100 \text{ }\mu\text{m}$; and

20 b) from 10 to 50 %w of a second particulate α -alumina having an average particle size (d_{50}) of from 1 to $10 \text{ }\mu\text{m}$; %w being based on the total weight of α -alumina in the mixture; and firing the mixture to form the carrier.

14. A process as claimed in claim 13, wherein the carrier has an alumina content of at least 95 %w, the mixture comprises:

25

a) from 65 to 75 %w, relative to the total weight of α -alumina in the mixture, of a first particulate α -alumina having an average particle size (d_{50}) of from 11 to $60 \text{ }\mu\text{m}$;

30 b) from 25 to 35 %w, relative to the total weight of α -alumina in the mixture, of a second particulate α -alumina having an average particle size (d_{50}) of from 2 to $6 \text{ }\mu\text{m}$;

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